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13. ABSTRACT (Maximum 200 words)

Optical hole burning is a high resolution spectroscopy technique that is used to characterize optical materials. It has applications in optical data storage. Rare-earth ion doped crystals, glasses; color centers and dye doped polymers are candidate materials for this purpose. Rare-earth ion doped glasses produce transient as well as persistent spectral holes. The nature of the hole burning depends on the glass preparation methods. Hole burning efficiency depends on the glass composition as well. We investigated persistent spectral hole burning studies in europium doped glasses such as sodium borates; silicates, borosilicates, germanates and tellurites. The hole stability as well as hole burning efficiency was investigated by varying the glass composition. Sodium silicate glasses did not retain more than one hole at a time, On the other hand hole burning was achieved with a mW power. Sodium borate glasses retained multiple holes but they required higher power (100x than silicates) to burn a hole. However multiple hole burning was achieved in sodium borosilicate glass at moderate powers. In borates, silicates and borosilicates hole burning occurred by a charge exchange between the excited Eu^{3+} ion and a neighboring Eu^{2+} ion or a defect. Hole burning efficiency also increased with the 23-abundance of Eu to some extent. However both photophysical as well as photochemical mechanisms were found to be responsible for hole burning in sodium germanate glass. The effect of Y^{3+} was investigated on hole burning. Y^{3+} increased the abundance of Eu^{2+} and also the hole burning efficiency. We also observed high temperature hole burning in europium doped sodium telluride glass.

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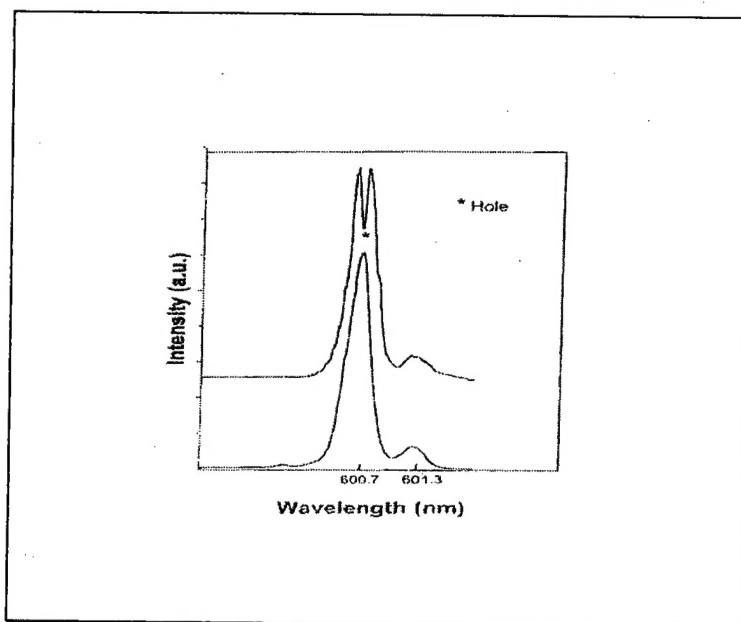


Final Technical Report

Preparation and characterization of high temperature hole burning materials



Grant # F49620-01-1-0328



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Table of contents	page #
Cover page	1
Personnel	3
Objective of the proposal	4
Summary	4
Salient features (or highlights) of the research	5
Sample preparation and characterization	5
Sodium borate glass	7
Sodium silicate glass	8
Sodium borosilicate glass	9
Sodium germanate glass	9
Sodium tellurite glass	10
Lead germanium niobate glass	10
Samarium doped sodium borate glass	10
Hole burning in color centers	11
Publications/manuscripts/presentations	12
Table 1: Comparison of Eu^{3+} doped glasses for hole burning	13
Appendix	14
1. Effect of the addition Y_2O_3 on PSHB in Eu doped sodium borate glass	
2. PSHB studies of F_2 color center in lithium fluoride	
3. PSHB studies of Eu doped sodium germanate glass	
4. PSHB in Eu doped sodium borosilicate glass	
5. PSHB in Eu, Y co-doped sodium silicate glass	
6. PSHB in Eu doped sodium tellurite glass	

Final Technical Report

Dates covered: April 15, 2001 to May 31, 2004

Title: Preparation and characterization of high temperature hole burning materials

Grant# F49620-01-1-0328

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Personnel: Four graduate students, a postdoctoral research associate and the principal investigator participated in this work.

(a) Graduate students: Three graduate students completed their M. S. thesis work and received their degrees. Another student is working for his M. S. thesis work.

(1) Ms. Elizabeth Schoolefield, M. S. (2003)

Thesis title: Persistent spectral hole burning studies of Eu^{3+} -doped sodium borate glasses. A copy was submitted to Dr. Pomrenke.

(2) Mr. William Conway III, M.S. (2003)

Thesis title: Persistent spectral hole burning studies in lithium fluoride color centers. A copy was submitted to Dr. Pomrenke.

(3) Mr. Sundar Rama Rao Bairavarasu, M.S. (2003)

Thesis title: Persistent spectral hole burning studies in Eu^{3+} -doped sodium silicate glasses. A copy was submitted to Dr. Pomrenke.

(4) At the moment Mr. Chandra Pulluru, a graduate student of Physics is working on his thesis work. He is pursuing his M. S. thesis work on germanate glasses.

(b) Research Associate: Dr. Rajamohan R. Kalluru was involved in this project from January 15, 2002 onwards.

Objective of the proposal

To prepare high temperature glasses and characterize their suitability for optical hole burning/memory.

Summary

Optical hole burning is a high resolution spectroscopy technique that is used to characterize optical materials. It has applications in optical data storage. Rare-earth ion doped crystals, glasses; color centers and dye doped polymers are candidate materials for this purpose. Rare-earth ion doped glasses produce transient as well as persistent spectral holes. The nature of the hole burning depends on the glass preparation methods. Hole burning efficiency depends on the glass composition as well. We investigated persistent spectral hole burning studies in europium doped glasses such as sodium borates, silicates, borosilicates, germanates and tellurites. The hole stability as well as hole burning efficiency was investigated by varying the glass composition. Sodium silicate glasses did not retain more than one hole at a time. On the other hand hole burning was achieved with a mW power. Sodium borate glasses retained multiple holes but they required higher power ($100\times$ than silicates) to burn a hole. However multiple hole burning was achieved in sodium borosilicate glass at moderate powers. In borates, silicates and borosilicates hole burning occurred by a charge exchange between the excited Eu^{3+} ion and a neighboring Eu^{2+} ion or a defect. Hole burning efficiency also increased with the abundance of Eu^{2+} to some extent. However both photophysical as well as photochemical mechanisms were found to be responsible for hole burning in sodium germanate glass. The effect of Y^{3+} was investigated on hole burning. Y^{3+} increased the abundance of Eu^{2+} and also the hole burning efficiency. We also observed high temperature hole burning in europium doped sodium telluride glass.

Salient features (or highlights) of the research

- We prepared inorganic glasses with Eu^{3+} and Eu^{2+} as dopants.
- Observed hole burning in europium doped sodium tellurite for the first time.
- Observed hole burning in europium doped sodium germanate for the first time.
- Observed hole burning in europium doped sodium borosilicate for the first time.
- Investigated the effect of Y^{3+} on hole burning in Eu -doped glasses.
- We had experimental evidence for photophysical hole burning.
- Observed hole burning in the F_2 center of LiF for the first time.
- Four graduate students and a postdoc participated in research.
- Prepared six manuscripts (2 were published and 3 have been communicated).

Sample preparation and characterization

Glasses were prepared by mixing appropriate chemicals and melting them in a box furnace or tube furnace. A typical concentration of the dopant ion was about 2mol%. Most of the chemicals were oxides except sodium carbonate. The purity of the chemicals was better than 99.9% and were obtained from Alfa-Aesar. A box furnace was used to make glasses in ambient air. A tube furnace was used to make glasses in a reduced atmosphere. Platinum, Platinum-Rhodium, Aluminum or Porcelain crucibles were used to heat the chemicals at high temperatures. Room temperature absorption spectrum was recorded with a CARY 3E spectrophotometer. Europium existed only in trivalent form for samples made in ambient air. Europium is present in divalent as well as trivalent form for samples made in a reduced atmosphere. The samples were cooled to 10K in a

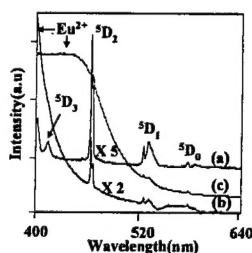
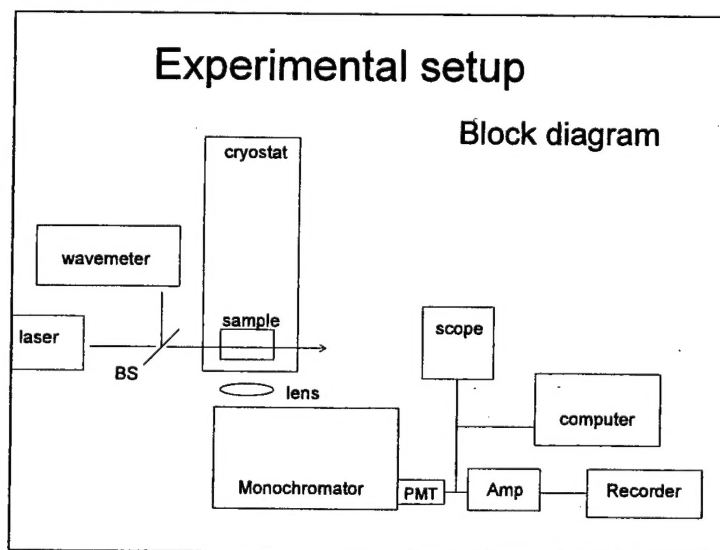


FIG.1, Room temperature absorption spectrum

closed cycle helium cryostat. A fiber coupled tungsten lamp was used to record low temperature transmission spectrum. Argon ion, Argon ion pumped dye laser (Spectra Physics Model 375B) and a Laser Science Nitrogen laser was used to excite luminescence from the material. Eu^{2+} emission is observed under Nitrogen laser excitation. A single dye laser was used to burn a hole and probe the



hole. A high power beam (typical power is 100mW) was used to burn a hole and a low power beam ($\sim 1\text{mW}$) was used to probe the hole. A computer controlled medium

resolution spectrometer was used to analyze the fluorescence. The spectrometer was fitted with a photomultiplier tube whose output was acquired by a computer. Excitation spectra as well as intensity versus time data were used to reveal hole burning.

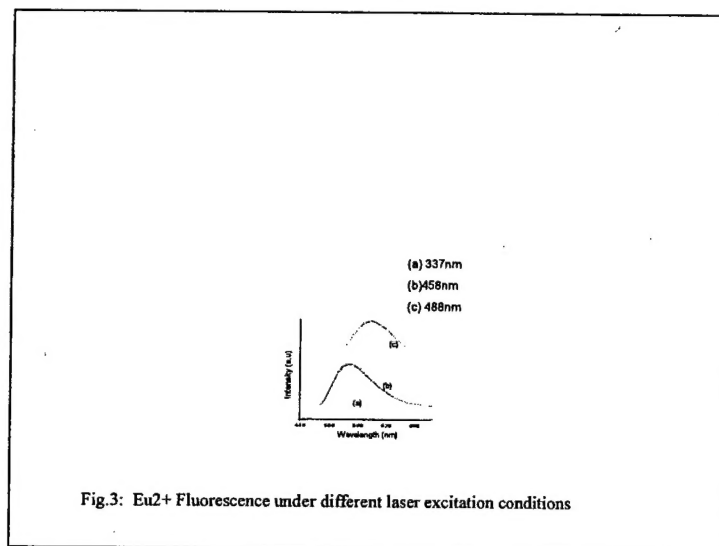


Fig.3: Eu²⁺ Fluorescence under different laser excitation conditions

Sodium borate glass

We prepared Eu³⁺ -doped Sodium borate glass by the melt quenching technique in ambient air, nitrogen atmosphere and reduced atmosphere. The glass composition is as follows: Na₂O (27%), B₂O₃(66%), Y₂O₃(5%), and Eu₂O₃ (2%). The chemicals were melted at 1400°C. Hole burning was observed only when the glass was made in a reduced atmosphere. Persistent holes were burned up to 100K. The ratio of inhomogeneous broadening to hole width is 40. When the sample was co-doped with 5% Y³⁺, hole burning was observed up to room temperature. Hole burning efficiency increased 18×. Holes lasted for longer than three hours. These results appeared in the Journal of Applied Physics 94, 2139-41 (2003). Sodium borate glasses required a few minutes of exposure to the laser beam to burn a hole. Hole burning efficiency was found to be higher when

the glass contains a higher percentage of Eu^{2+} which was the case when the glass was melted in a reduced atmosphere. However the presence of Y^{3+} enhanced the concentration of defects as well as Eu^{2+} . Hence the hole burning efficiency increased.

Sodium silicate glass

We made a Eu^{3+} -doped sodium silicate glass in ambient air, nitrogen atmosphere and reduced atmosphere. The base glass composition is SiO_2 (45.2%), $\text{NaO}_{1/2}$ (48.8%), $\text{YO}_{3/2}$ (6%). The chemicals were melted at 1550°C . glass was melted at Even in this glass we observed hole burning only when the glass was melted in a reduced atmosphere. Intensity versus time plot revealed hole burning up to 250K. This glass does not retain more than one hole when a constant power is used to burn holes. However if the laser power and time are reduced for successive holes the material retains about four holes. When 5% Y^{3+} was added to the sample we were able to burn deeper holes in about 30 seconds with 10mW laser. We were able to burn up to 7 holes in the co-doped glass. Intensity versus time revealed hole burning up to 300K. This is a significant improvement in the design of hole burning materials. The addition of Yttrium added stability to holes. These results have been communicated to Journal of Luminescence.

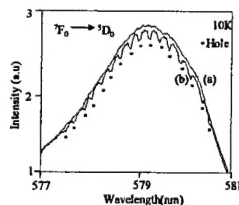


Fig.4: Multiple hole burning in Eu doped Sodium borosilicate glass

Sodium borosilicate glass

We made a borosilicate glass in a reduced atmosphere at 1450°C with the following composition: Na_2CO_3 (30%), B_2O_3 (34%), SiO_2 (34%), and Eu_2O_3 (2%). The hole stability increased. Hole burning occurred in about 20 s at moderate laser powers. In other words we are able to burn multiple holes and the material retained all the holes. The exposure time and laser power required to burn a hole are less when compared to borate glass and the holes are more stable when compared to silicate glass. Intensity versus time revealed hole burning up to 250 K. Intensity versus time plot showed evidence of room temperature hole burning. The sample retained holes (without any significant change) even if the holes are burned at 0.1 nm interval. A manuscript has been submitted to Journal of Applied Physics.

Sodium germanate glass

We made europium doped sodium germanate glass in ambient air as well as reduced atmosphere. A typical composition is Na_2O (21%), GeO_2 (78%), and Eu_2O_3 (1%). The glass melted at 1150-1200°C. Hole burning was observed even though the glass was made in ambient air. Hole burning efficiency increased 85% when the glass was made in a reduced atmosphere. Even a few mW of laser power was enough to burn a hole. Both photochemical as well as photophysical hole burning occurred in this material. A manuscript has been submitted to Journal of Applied Physics.

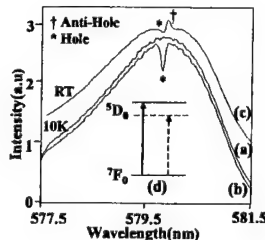


Fig.5: Hole burning at 293K and 10K in Eu doped Sodium germanate glass

Sodium tellurite glass

We made a europium doped sodium telluride glass by melting it at 850°C. The glass composition is as follows: TeO_2 (69%), Na_2CO_3 (27%), Y_2O_3 (3%), and Eu_2O_3 (1%). The glass is transparent when it was made in ambient air and was completely opaque when it was melted in a reduced atmosphere. The material was deficient in oxygen. Persistent holes were burned even though the glass was made in ambient air. Multiple hole burning was possible and the material retained all the holes. A manuscript is in preparation.

Lead germanium niobate glass

We also made europium doped niobates. In this material we were able to burn holes when the glass was melted in ambient air. When the glass was melted in a reduced atmosphere the glass became opaque and we could not pursue optical studies. Further work is in progress to improve the material characteristics.

Samarium doped sodium borate glass

WE also made a sodium borate glass doped with samarium. When the glass was made in ambient air, only Sm^{3+} peaks were detected. However when the sample was

made in a reduced atmosphere both Sm^{2+} and Sm^{3+} formed in the material. Such materials are useful for gated hole burning studies.

Hole burning in color centers

We burned persistent spectral holes at 600.7nm peak belonging to the F_2 center in LiF crystal. The broad band at 645nm contains emission from several centers. Lifetime measurements under 5-ns pulsed nitrogen pumped dye laser excitation revealed spectral overlap from several centers. Temporal measurements revealed two short lived signals (8 and 20ns) and a two long lived signals (100 and 200 ns). A paper was published in Journal of Luminescence 107, 249-255 (2004).

Publications/manuscripts/presentations (see Appendix for copies)

- (1) Effect of the addition Y_2O_3 on persistent spectral hole burning studies of Eu^{3+} doped sodium borate glass, Rajamohan R. Kalluru, Elizabeth Schoolfield and B. R. Reddy, J. Appl. Phys. 94, 2139-2141 (2003).
- (2) Persistent spectral hole burning studies in the F_2 color centers in lithium fluoride, W. Conway and B. R. Reddy, J. Luminescence 107, 249-255 (2004).
- (3) Persistent spectral hole burning studies of europium doped sodium germanate glass, R. R. Kalluru, C. R. Pulluru and B. R. Reddy, J. Appl. Phys. (submitted).
- (4) Persistent spectral hole burning in europium doped sodium borosilicate glass, R. Kalluru, C. Pulluru and B. R. Reddy, J. Appl. Phys. (submitted).
- (5) Persistent spectral hole burning in Eu^{3+} , Y^{3+} codoped sodium silicate glass, R. Kalluru, S. Bairavarasu and B. R. Reddy, J. Luminescence (submitted).
- (6) Persistent hole burning studies of europium doped sodium telluride glass, R. Kalluru, C. Pulluru and B. R. Reddy (manuscript in preparation).
- (7) Persistent spectral hole burning studies in lithium fluoride color centers, W. Conway and B. R. Reddy, Proceedings of 8th International Meeting on Hole Burning and Single Molecule Spectroscopies: Science and Applications (July 27-31, 2003, Bozeman, Montana) page 65.
- (8) Optical hole burning in europium doped borate glasses, Rajamohan R. Kalluru, Elizabeth Schoolfield and B. R. Reddy, Proceedings of 8th International Meeting on Hole Burning and Single Molecule Spectroscopies: Science and Applications (July 27-31, 2003, Bozeman, Montana) page 66.

Table 1. Comparison of Eu^{3+} -doped glasses for hole burning (ES: excitation spectrum and IVT: intensity versus time).

Parameter	Sodium silicate glass	Sodium borate glass	Sodium borosilicate glass	Sodium germanate glass	Sodium telluride glass
Glass Composition	$\text{Na}_2\text{O}_{1/2}$ (51.8%), SiO_2 (48.2%) Eu_2O_3 (1.5%)	Na_2O (27%), B_2O_3 (66%), Eu_2O_3 (2%) Y_2O_3 (5%)	Na_2O_3 (30%) B_2O_3 (34%) SiO_2 (34%) Eu_2O_3 (2%)	Na_2O (21%), GeO_2 (78%), Eu_2O_3 (1%)	Na_2O (27%), TeO_2 (69%), Y_2O_3 (3%), Eu_2O_3 (1%)
HB temperature maximum	250K(IVT)	300K(IVT)	250K (ES) 293K(IVT)	293K(ES)	200K
#holes at a spot	4 (or 7) see note (a)		16 (at 0.1nm interval)	10 (or 16) see note (b)	14
Hole depth	27%	11(or 24%) see note (c)	18%	18%	31%
$\Gamma_{\text{inh}}/\Gamma_{\text{hom}}$	31	40	27	28	15
Thermal cycling (100K for 5 minutes)	40% hole erased		44% hole erased		

Notes: (a) Number of holes burned increased from 4 to 7 when 5% Y_2O_3 was added to the glass.

(b) Number of holes increased from 10 to 16 when the sample contains 3% Y_2O_3 .

(c) Hole depth increased from 11 to 24% when 5% Y_2O_3 was added to the glass.

APPENDIX

Copies of the publications and manuscripts

**PERSISTENT SPECTRAL HOLE BURNING STUDIES OF Eu^{3+} -DOPED
SODIUM BORATE GLASSES**

by

ELIZABETH ISRAEL SCHOOLFIELD

A THESIS

**Submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Applied Physics
in the School of Graduate Studies**

**Alabama Agricultural and Mechanical University
Normal, Alabama 35762**

May 2003

Submitted by ELIZABETH ISRAEL SCHOOLFIELD in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE specializing in APPLIED PHYSICS.

Accepted on behalf of the Faculty of the Graduate School of the Thesis

Committee:

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A. Tan
Shelia Foster-Stinson
B. M. Dy Major Advisor

W. R. Kelly Dean of the Graduate School
6/6/03 Date

**PERSISTENT SPECTRAL HOLES BURNING STUDIES IN
LITHIUM FLUORIDE COLOR CENTERS**

By

William Conway III

A Thesis

Submitted in partial fulfillment of the requirements

For the degree of Master of Science

In the Department of Physics

In the School of Graduate Studies

Alabama Agricultural and Mechanical University

Normal, Alabama 35762

July 7, 2003

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for the degree of MASTER OF SCIENCE in APPLIED PHYSICS specializing in the
area of OPTICS/ LASERS.

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10/17/03

Date

**PERSISTENT SPECTRAL HOLE BURNING STUDIES OF Eu^{3+} -DOPED
SODIUM SILICATE GLASSES**

By

SUNDAR RAMA RAO BAIRAVARASU

A THESIS

**Submitted in partial fulfillment of the requirements
for the degree of Masters of Science in the
Department of Physics
in the School of Graduate Studies.**

**Alabama Agricultural & Mechanical University
Normal, Alabama 35762**

July 16, 2003

Submitted by *SUNDAR RAMA RAO BAIRAVARASU* in partial fulfillment of the requirements for the degree of *MASTERS OF SCIENCE* in *APPLIED PHYSICS* specializing in Optics/Lasers.

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9/18/03

Date

Effect of the addition Y_2O_3 on persistent spectral hole burning in europium doped sodium borate glass

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(Received 30 September 2002; accepted 15 May 2003)

Persistent hole burning is observed in a europium doped sodium borate glass from 10 to 100 K. Hole burning efficiency increased $18\times$ when 5% yttrium oxide was added to the glass mixture. Hole burning was observed up to 300 K in Eu^{3+} , Y^{3+} Co-doped glass. © 2003 American Institute of Physics. [DOI: 10.1063/1.1589598]

Optical hole burning is a high resolution spectroscopy technique used to investigate zero-phonon lines (ZPL). It has applications in high density optical data storage.¹ The information storage capacity depends on the ratio of the inhomogeneous to homogeneous linewidths. Homogeneous linewidth depends on the relaxation times of the levels involved. Inhomogeneous linewidth depends on the disorder in the material. Also, the material should exhibit hole burning at temperatures higher than those achieved using cryogenics to have any commercial applications. Hence, there is a need to design and characterize materials for high temperature and high capacity hole burning applications. Majority of the rare-earth ion doped crystals facilitate transient hole burning¹ where the hole lifetime is less than the lifetime of the levels involved. However, in Pr^{3+} doped glasses persistent spectral hole burning (PSHB) was observed where the hole lasts for time that is much longer than the lifetimes of the levels involved,² and this was due to rearrangement of the local environment of the excited ions. This phenomenon is termed photophysical hole burning and facilitates PSHB that is useful for long-time information storage. Later on PSHB was observed in several types of glasses.^{3–14} The past studies also indicate that the actual hole burning mechanism depends on the glass composition and preparation methods. For example, in Eu^{3+} -doped sol-gel glasses persistent hole burning was observed due to rearrangement of the OH bonds surrounding the excited optical centers.⁶ Room temperature photochemical hole burning was observed in Eu^{3+} doped sodium borate glasses that were made in a reducing atmosphere.^{5,15} The suggested mechanism was the exchange of a charge between Eu^{3+} and Eu^{2+} . Optical hole burning was also observed by the exchange of a charge between the optical center and a defect that was created during the material preparation¹⁶ and/or a partially reduced dopant ion.¹⁷ Our current effort is to develop materials that facilitate efficient hole burning at higher temperatures. The effect of Y^{3+} on the hole burning in a Eu^{3+} -doped borate glass is discussed here.

We made the sodium borate glass in our laboratory with the following composition: Na_2O (33 mol %), B_2O_3 (65 mol %), and Eu_2O_3 (2 mol %). The starting chemicals are all oxides except sodium carbonate. Their purity is better than

99.9%. These chemicals were mixed in a porcelain mortar and then heated in a box furnace for an hour in the range 800–1100 °C. Later on it was melted in a reducing atmosphere at 1400 °C for an hour. For this purpose a tube furnace was used. A mixture of 95% nitrogen and 5% hydrogen was passed through the furnace at a pressure of 20 PSI. The resulting melt was poured in an alumina mold and cooled to room temperature. We made another glass that is codoped with Y^{3+} , in a reducing atmosphere, having the following composition: Na_2O (27 mol %) + B_2O_3 (66 mol %) + Y_2O_3 (5 mol %) + Eu_2O_3 (2 mol %). Both the materials are transparent and exhibit a light tint of yellow color. The materials were polished to minimize scattering. Room temperature absorption spectra were recorded using a CARY3E spectrophotometer. Low temperature absorption and fluorescence measurements were made using a medium resolution spectrometer (Acton Research Corporation, model SpectraPro-500). The sample was cooled to 10 K in a closed cycle cryostat (Janis, model CCS-150). A tungsten halogen lamp (Ocean Optics, model LS-1) was used for low temperature transmission measurements. The transmitted light was collected by a fiber whose output is coupled to the entrance slit of a monochromator. In fluorescence measurements the sample was exposed to a dye laser beam or Ar^+ laser beam. The emitted light was collected at right angles to the incident beam direction by a lens and then imaged on to the entrance slit of the monochromator which was equipped with a Hamamatsu model R928 photomultiplier tube (PMT). The PMT output was acquired by a computer for further processing. An excitation spectrum was recorded by monitoring the emission intensity at 612 nm and simultaneously sweeping the laser frequency to cover the whole zero-phonon transition.

The absorption spectrum revealed peaks at 393 ($^7F_0 \rightarrow ^5D_3$), 465 ($^7F_0 \rightarrow ^5D_2$), 525 ($^7F_0 \rightarrow ^5D_1$), and 579 nm ($^7F_0 \rightarrow ^5D_0$). Low temperature absorption also revealed the same peaks (not shown). On resonantly exciting the 5D_0 level by a dye laser whose linewidth is 60 GHz, fluorescence occurred at 590–600 ($^5D_0 \rightarrow ^7F_1$), 612 ($^5D_0 \rightarrow ^7F_2$), 653 ($^5D_0 \rightarrow ^7F_3$), and 703 nm ($^5D_0 \rightarrow ^7F_4$). By monitoring the fluorescence at 612 nm an excitation spectrum was recorded at 10 K which revealed the ZPL $^7F_0 \rightarrow ^5D_0$ whose peak maximum is at 579 nm having a full width at half maximum

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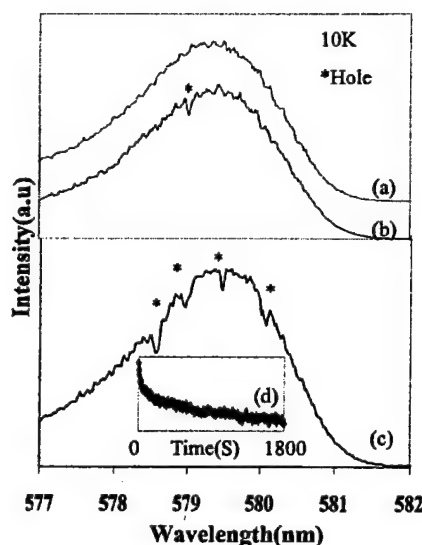


FIG. 1. Low temperature excitation spectrum of 612 nm emission before (a) and after (b) hole burning observed in Eu^{3+} -doped sodium borate glass. (c) Multiple hole burning in Eu^{3+} , Y^{3+} codoped glass. Inset (d) shows emission intensity vs time during the hole formation, observed in Eu^{3+} , Y^{3+} codoped sample.

of 2.1 nm (or 62.6 cm^{-1}) [Fig. 1(a)]. The ZPL was found to broaden at higher temperatures. The laser beam was focused to a spot size of about $30 \mu\text{m}$. To burn a hole the sample was exposed to the laser for 30 min with an irradiance of 12.3 kW/cm^2 . The laser power was reduced by a factor of 80 and then an excitation spectrum was recorded by scanning same laser frequency. The resulting scan revealed a hole in the excitation spectrum [Fig. 1(b)]. There is no noticeable change in the hole feature even after 3 h at 10 K. However, if the sample temperature is increased to 70 K for 10 min, and cooled back to 10 K later on, 90% of the hole was erased. In other words these holes are unstable thermally. By changing the laser frequency we burned holes at several different wavelengths within the absorption spectrum. No anti-holes were detected. At 10 K the hole width is $\sim 1.8 \text{ cm}^{-1}$, which is limited by the laser linewidth. Hole width broadened to 4 cm^{-1} at 100 K. The holes are $\sim 11\%$ in depth when the sample was exposed for 30 min with an intensity of 12.3 kW/cm^2 . When the sample temperature was higher than 100 K the holes were not conspicuous. We did not perform spectral subtraction to unravel the hole. The ratio of inhomogeneous broadening to the hole width is ~ 30 . This ratio is small because of the large laser linewidth used in our experiments. The ratio will be much higher if a narrow linewidth laser is used.

In the codoped glass (which contains Y_2O_3) multiple hole burning was detected very easily [Fig. 1(c)]. During the hole burning period the emission intensity decreased as expected due to a continuous decrease in absorption [Fig. 1(d)]. In this sample, 24% hole depth was achieved, for 30 min exposure at an intensity of 4.9 kW/cm^2 . In other words deeper holes were burnt in the codoped sample with less exposure. The hole depth did not change much even if the laser intensity was increased by a factor of 2. The ratio of

inhomogeneous broadening to hole width is ~ 40 . The hole burning efficiency is given by¹⁸

$$\eta = \frac{dT/dt}{(I/h\nu)\sigma T_0(1-T_0-R_0)}, \quad (1)$$

where dT/dt is the initial slope in the transmission versus time plot, I is the intensity of the laser beam in the sample, h is the Planck's constant, ν is the laser frequency, σ is the absorption cross section, T_0 is the initial transmission, and R_0 is the reflection loss from the sample surface. R_0 is estimated by measuring the loss at a wavelength, 590 nm that is not absorbed by the sample. During the hole burning process the transmission increases and the emission decreases at the same rate. Hence, dT/dt is obtained from the emission intensity versus time plot. In our samples some of the Eu^{3+} ions are reduced to Eu^{2+} (clarified later on). So the estimation of Eu^{3+} concentration as well as the absorption cross section will not be accurate. Moreover, σ is not expected to vary significantly between the two samples. So Eq. (1) has been modified to describe the relative hole burning efficiency, as

$$\frac{\eta_2}{\eta_1} = \frac{(dT/dt)_{02}I_{01}T_{01}(1-T_{01}-R_{01})}{(dT/dt)_{01}I_{02}T_{02}(1-T_{02}-R_{02})}, \quad (2)$$

where subscripts 1 and 2 refer to the Eu^{3+} -doped and Eu^{3+} , Y^{3+} Co-doped glasses, respectively. The relative efficiency is estimated as $\eta_2/\eta_1 = 18$ with $(dT_{02}/dt)/(dT_{01}/dt) = 11.1$, $I_{01}/I_{02} = 1.15$, $T_{01}/T_{02} = 1.0$, and $(1-T_{01}-R_{01})/(1-T_{02}-R_{02}) = 1.45$. The efficiency is higher in the codoped glass because dT/dt is higher and requires less power to burn a hole.

Next we tried to understand the role played by Y^{3+} in the hole burning process. For this purpose absorption spectral recordings are compared in Fig. 2 for the doped and undoped samples and for glasses made in a reducing atmosphere as well as ambient air. The glass made in air atmosphere exhibited sharp peaks of Eu^{3+} at 393 and 465 nm superimposed on a broad background [curve (a) in Fig. 2]. The maximum absorption of the background at 350 nm is 3.5 in optical density (o.d.). When a glass of the same material is made in a reducing atmosphere with 2 mol % Eu^{3+} , there is a broad absorption peaking at about 400 nm (o.d. = 6.0) and extending up to 450 nm [curve (b)]. A small peak at 465 nm (Eu^{3+}) is still visible. The Eu^{3+} peak intensity in curve (b) is smaller than that in curve (a) (Fig. 2). It implies that some of the Eu^{3+} ions are reduced to Eu^{2+} . That is why the absorption at 400 nm increased by three orders of magnitude. In a glass doped with Eu^{3+} (2 mol %) and Y^{3+} (5 mol %) the broad absorption extends up to 490 nm [curve (c)] and the Eu^{3+} peaks are not visible. This clearly indicates that a larger number of Eu^{3+} ions are reduced to Eu^{2+} in the glass codoped with Y^{3+} . In the reduction process the Eu^{3+} gains an electron from the host glass. The probability for Eu^{3+} to gain an electron increases when the glass is codoped with Y^{3+} because the latter was more effective in dispersing the rare-earth more uniformly.^{14,19} This is also supported by the fact that the absorption coefficient of Eu^{3+} at 580 nm decreased from 0.2 cm^{-1} in Eu^{3+} doped glass to 0.08 cm^{-1} in Eu^{3+} , Y^{3+} codoped glass, both being prepared under similar

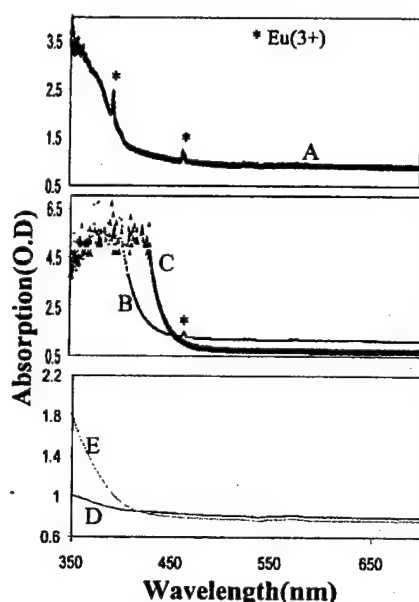


FIG. 2. Room temperature absorption spectra of (a) Na_2O (34 mol %) + B_2O_3 (65 mol %) + Eu_2O_3 (1 mol %). The narrow peaks at 393 and 465 nm are Eu^{3+} transitions. (b) Na_2O (33 mol %) + B_2O_3 (65 mol %) + Eu_2O_3 (2 mol %), (c) Na_2O (27 mol %) + B_2O_3 (66 mol %) + Y_2O_3 (5 mol %) + Eu_2O_3 (2 mol %), (d) Na_2O (33.6 mol %) + B_2O_3 (66.4 mol %), and (e) Na_2O (27.5 mol %) + B_2O_3 (67.4 mol %) + Y_2O_3 (5.1 mol %). Sample (a) was melted in air atmosphere and the others [(b), (c), (d), and (e)] were melted in a reducing atmosphere.

conditions. Also the hole depth is deeper in the codoped glass, which has higher Eu^{2+} concentration. In other words higher the Eu^{2+} content deeper the hole. This is also in agreement with the observations of Fujita *et al.*¹⁵ for low concentrations. A comparison is made of the absorption spectra of undoped glasses in curves (d) and (e) (Fig. 2), both prepared in a reducing atmosphere. Curves (d) and (e) reveal a background absorption (o.d.=0.8) from 400 to 700 nm, which is partly due to imperfect polishing. However, from 350 to 400 nm the absorption of sample (e) is much higher (at 350 nm, o.d.=1.8) than that in curve (d) (o.d.=1.0). This indicates that certain defects are produced in the glasses and their concentration is much higher when the glass contains Y^{3+} . These defects are effective in reducing the Eu^{3+} – Eu^{2+} . More noticeably, the UV absorption of Eu^{2+} broadened to the blue region [curve (c)].

All the observations clearly indicate that the optically excited centers are undergoing some type of charge exchanges with the traps, which are a combination of Eu^{2+} and other defects produced in the reduction process.^{5,15–17} This

prediction is supported by the fact that no holes were observed in glasses made under ambient air or nitrogen atmosphere. The OH bonds are absent in high temperature glasses made under inert atmosphere and so they do not contribute to the hole burning mechanism.

In summary, we prepared Eu^{3+} -doped and Eu^{3+} , Y^{3+} Co-doped sodium borate glasses and demonstrated persistent spectral hole burning in the ${}^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} . We did not observe hole burning for glasses made in ambient air or nitrogen atmosphere. The minimum power required to burn a hole in the yttrium codoped glass is about one third of that required for the other glass. Holes could be burnt easily up to 300 K in codoped samples and up to 100 K in the other sample. The hole burning efficiency and hole density of the codoped glass are, respectively, 18× and 20% higher than those measured for the other glass. The hole burning occurs due to charge transfer between the Eu^{3+} ions and the traps (Eu^{2+} and other defect centers) which are formed during the preparation stages.

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Persistent spectral hole burning studies of F_2 color center in lithium fluoride

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Abstract

Color centers were produced in lithium fluoride (LiF) single crystal by gamma rays. Low-resolution transmission and emission measurements of LiF revealed several zero-phonon transitions. High-resolution excitation spectrum revealed three closely spaced zero-phonon lines at 601 nm belonging to different sites. F_2 center is the dominant site. Optical hole burning studies were performed in all these sites. Hole kinetics are performed as a function of temperature, laser power and time. We have demonstrated experimentally the production of light-induced centers.

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Keywords: Optical hole burning; F_2 color center; Zero phonon transitions; High-resolution spectra; Laser-induced color center; Photoionization; LiF

1. Introduction

Lithium fluoride (LiF) is a transparent material that produces color centers on exposure to high-energy radiation such as X-rays, gamma rays or electrons [1]. Conventional spectroscopy of this material was done extensively [1–6]. The nature of the induced centers depends on the type of radiation and dosage used as well as on the temperature of the material during exposure [7–9]. Most of the centers are unstable at room temperature except for the F_2 center. Tunable lasers were also developed in the visible and near-infrared regions. Though the material was known to exhibit broad absorption features the zero-

phonon transitions are not conspicuous most of the time for every type of center due to spectral overlap from different color centers. The past studies also indicated that some centers undergo photoionization or another type of photochemical change [2,3,7]. Any species that undergoes photochemical change has its own energy levels different from that of the parent species. So such systems may be useful for optical data storage because they exhibit persistent hole burning. Spectral hole burning is a high-resolution spectroscopic technique used to investigate zero-phonon lines (ZPL) [10]. ZPLs are very broad due to crystal field inhomogeneities. For practical applications the material should exhibit hole burning at higher temperatures. The information storage capacity depends on the ratio of inhomogeneous to homogeneous line widths. Hole burning was observed in LiF at 834 nm (R' center or F_3^-) [11] and 1.04 μm

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(F_2^- center) [12]. Here we are reporting hole burning in the F_2^- center and two other F -aggregate centers whose ZPLs are located at 601 ± 1 nm for the first time to our knowledge. We obtained some more interesting results in this material.

2. Experimental

LiF sample used in the study was obtained from Optovac, Inc. The sample size is 1-cm^3 . Color centers were produced by exposing the material to gamma radiation at room temperature. The sample color is that of a burnt orange. Room temperature absorption spectrum was recorded using a Cary3E spectrophotometer. A block diagram of the experimental setup is shown in Fig. 1. The sample is cooled to low temperatures in a closed cycle cryostat (Janis Model CCS-150) that produces temperatures ~ 8 K. Sample temperature is monitored using a Lakeshore Model 321 temperature controller. Sample transmission and emission measurements were made using a medium resolution monochromator (Acton Research Corporation Model Spectrapro-500) that is equipped with a Hamamatsu Model R928 photo-

multiplier tube (PMT). An Argon ion pumped dye laser (Spectra Physics Model 375B) was used to induce fluorescence from the sample, burn holes and record excitation spectra. The dye laser line width is ~ 60 GHz. For lifetime measurements a nitrogen pumped dye laser (Laser Science Model 337ND-S and DUO-220) was used. It was operated at 20 Hz. Its pulse width is ~ 5 ns. The PMT output was acquired by a multichannel scaler (Stanford Research systems Model SR430). Lifetimes were derived by fitting the decay curves to single exponentials. Holes were burned with a high power laser beam ~ 60 – 120 mW and holes were probed with a low power beam of ~ 1 – 2 mW. In the excitation spectral recordings emission intensity at 645 nm was monitored by simultaneously sweeping the laser frequency to cover the whole ZPL centered at 601 nm.

3. Results and discussion

3.1. Absorption and emission spectra

A room temperature absorption spectrum revealed a strong absorption at 445 nm (M-center: F_2^- and F_3^+ centers absorb at this wavelength) (Fig. 2). The peak is very broad having a full-width at half-maximum (FWHM) of 76.4 nm (or

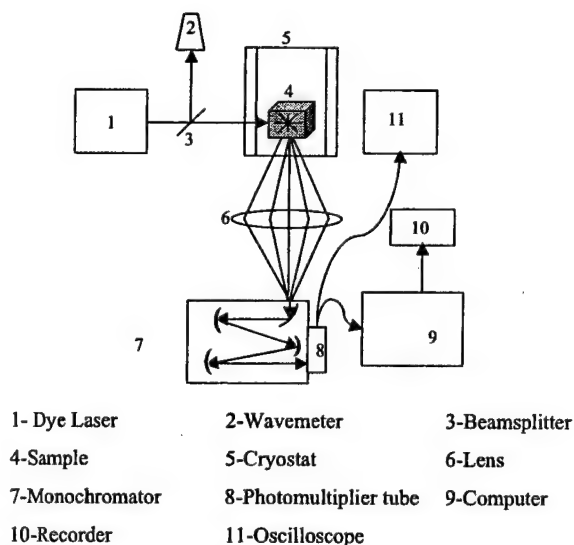


Fig. 1. Block diagram of the experimental setup.

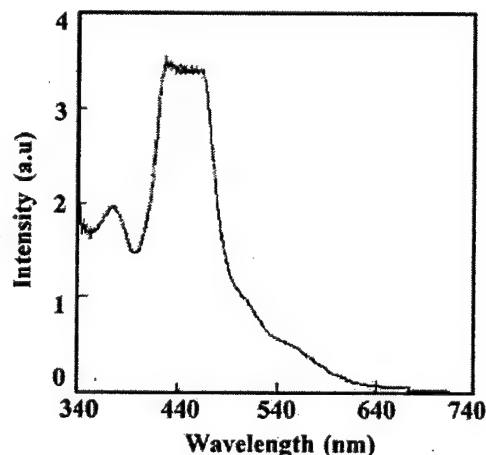


Fig. 2. Room temperature absorption spectrum of LiF color centers.

3883 cm^{-1}). Its optical density is 3.43 and the corresponding absorption coefficient is 7.9 cm^{-1} . There is also a smaller peak at 375 nm whose optical density is 1.94 and the corresponding absorption coefficient is 4.5 cm^{-1} . The smaller peak was identified as R_2 band [5,6]. The absorption spectrum has a long tail that extends up to 660 nm having very weak shoulders at 509 and 550 nm . Transmission spectrum of the sample at 10 K was recorded using a charge coupled device (CCD) camera. One such spectrum is shown in Fig. 3. It reveals zero-phonon transitions at 834 (F_3^-), 600.7 (F_2), 562.1 (N) and 524.3 nm (N_1), where the symbols in the parentheses indicate the types of centers. The spectrum shown in Fig. 3 was recorded in two segments and joined together, which is revealed by a discontinuity at 615 nm . All these centers were known to occur in LiF [1–9]. The material exhibited bright orange emission on exposure to Ar ion or a dye laser even at room temperature. The zero phonon transitions at 600.7 and 834 nm were observed in the fluorescence spectrum also at 10 K . The past studies indicated that only the F_2 center was stable at room temperature and its emission was observed at

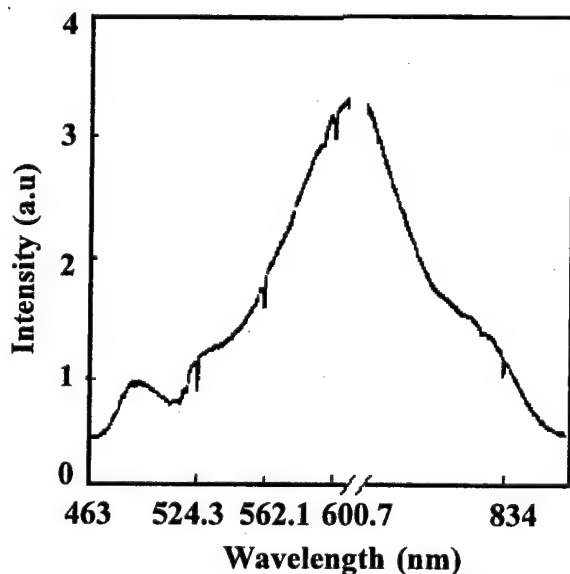


Fig. 3. Transmission spectrum of LiF color centers. Sharp lines at 834 , 600.7 , 562.1 and 524.3 nm are the ZPLs. Sample temperature was maintained at 10 K .

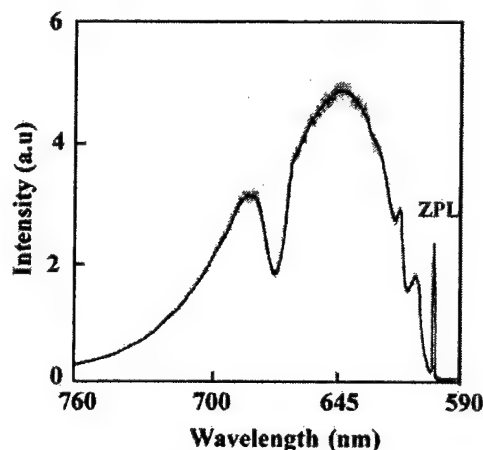


Fig. 4. Fluorescence spectrum of the sample reveals a sharp ZPL at 601 nm . The sample temperature was maintained at 10 K . The broad dip at 670 nm is due to a grating defect.

670 nm [13]. A 580 nm dye laser was used to excite the phonon band of the F_2 transition. The resulting emission peaked at 645 nm having a FWHM of 75.2 nm (1813 cm^{-1}) (Fig. 4). The dip at 670 nm is due to a grating defect. The fractional amount of light emitted in the zero phonon transition is about $\sim 7 \times 10^{-3}$. For lifetime measurement the sample was excited by a 5 ns pulsed dye laser of wavelength 600 nm and emission at 645 nm was measured. When the initial portion of the lifetime data was expanded and analyzed carefully it revealed a short decay time $\sim 18\text{ ns}$ followed by the long-decay time. The short-decay time agrees with that of F_2 center [13]. So the ZPL at 600.7 nm (peak A) is assigned to the F_2 center. In addition, there is a delayed emission signal whose lifetime is $\sim 180\text{ ns}$. This clearly supports the idea that there is spectral overlap from different color centers in the red region which is further clarified in Section 3.3.

3.2. ZPLs and optical hole burning

A high-resolution excitation spectrum of the 645 nm emission revealed a strong peak at 600.7 nm and a weak peak at 601.3 nm (identified by A and B in Fig. 5) at 10 K . Both the peaks are very stable at low sample temperature. These zero-phonon transitions were not observed in the past.

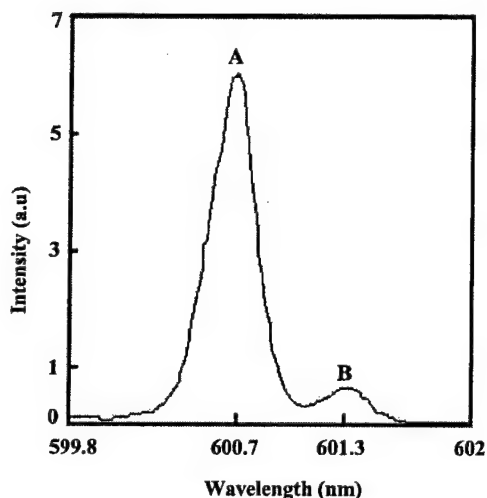


Fig. 5. Excitation spectrum of LiF reveals two sharp peaks (ZPLs) at 600.7 and 601.3 nm (peaks A and B). Fluorescence at 645 nm was monitored to record the spectrum. The sample temperature was maintained at 10 K.

The types of color centers produced and their relative abundance depend on the preparation methods. Moreover, color centers were produced in our sample about 12 years back. After all these years only the long-lived centers remained in the sample. As a result, the spectral overlap from several other short-lived centers was eliminated. This could be another reason why we were able to detect many ZPLs belonging to different centers in this material. The ZPL was recorded as a function of temperature in the excitation spectrum (Fig. 6). The F_2 center line width varied from 5.3 cm^{-1} (10 K) to 34 cm^{-1} (80 K). The peak features are evident up to 100 K. For temperatures higher than 100 K the inhomogeneous line broadening is too large and the ZPL does not appear. We also tried to burn holes in this transition. When the laser beam intensity on the sample was less than 3.9 kW/cm^2 hole burning was not obvious even for long exposures. However, when the laser intensity was exceeded 3.9 kW/cm^2 a hole was burned in the excitation spectrum (Fig. 7). The fact that the holes are burnt only at high powers indicates that at least two photons are involved in the hole burning process. Previous investigations [7,14] revealed that F_2 center ionization occurred by

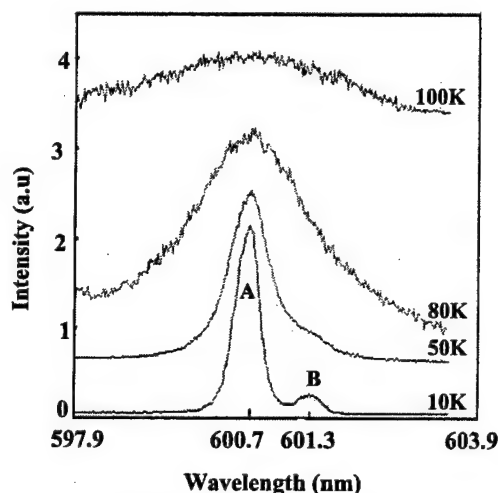


Fig. 6. Temperature dependence of F_2 center inhomogeneous profile in LiF.

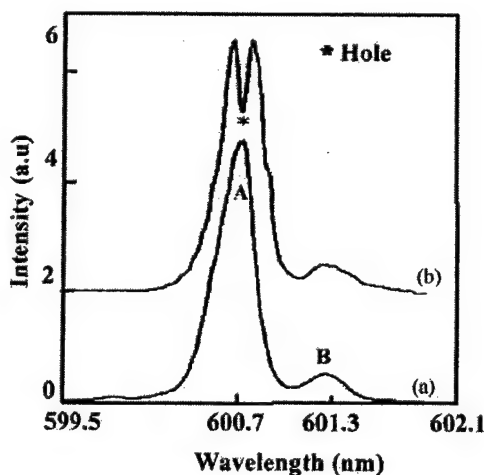


Fig. 7. Excitation spectra of LiF color center recorded (a) before and (b) after hole burning in the ZPL of F_2 color center. Fluorescence at 645 nm was monitored.

two-photon absorption. We believe that the same phenomenon is taking place in our sample at high-laser powers. Even when the laser power is increased $3\times$ no anti-holes were detected. We could achieve a hole depth of $\sim 30\%$ very easily. We were able to burn several holes within the inhomogeneous profile by changing the burning laser frequency. All holes (identified by an * in

peak profiles A and B) existed simultaneously (Fig. 8). At 10 K the hole retained its depth without any degradation even after 6 h. However, when the sample temperature was increased the hole depth was found to decrease and width increased. We were able to burn holes for sample temperatures less than 40 K. These holes were obvious to the naked eye and there was no need

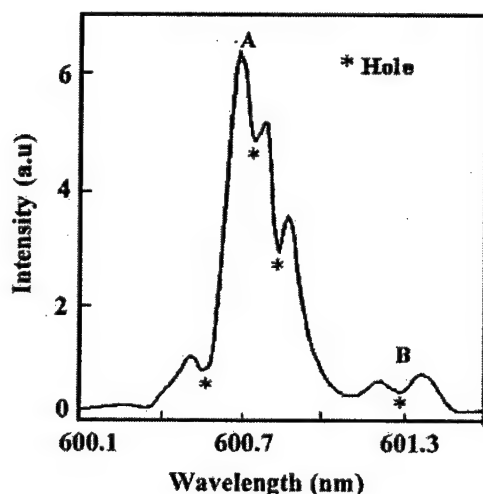


Fig. 8. Excitation spectrum reveals multiple holes in LiF color centers.

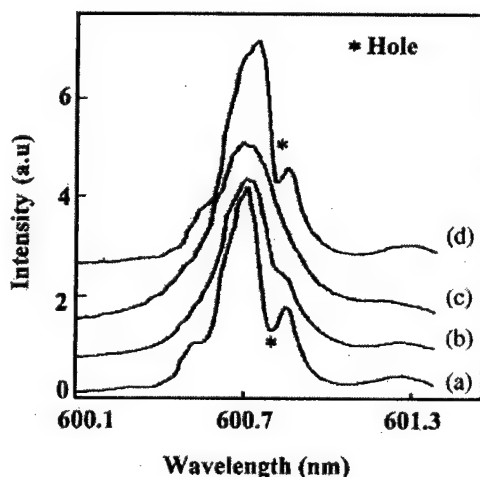


Fig. 9. Excitation spectra recorded as a function of sample temperature after a hole was burned in the ZPL: (a) 10 K (b) 40 K (c) 70 K and (d) 10 K.

for algebraic manipulation of the spectra. Another interesting observation is that the sample retained the hole even though its temperature was recycled. The curve (a) in Fig. 9 shows a spectrum where a hole was burnt at 10 K. When the sample temperature was increased to 70 K the hole disappeared completely (see curve (c)). However, when the sample was cooled back to 10 K the hole reappeared (curve (d)). The same behavior was seen even if the sample temperature was increased to 100 K. However, if the sample temperature was maintained at 200 K or above for 10 min the hole completely erased. In our measurements the hole width is ~ 100 GHz, which is approximately twice that of the laser line width.

3.3. Laser-induced color center

We also tried to monitor the emission intensity during the hole formation. No change in emission intensity was observed. This is because of the nature of the hole burning mechanism. In this sample, holes are burnt by photoionization of sites selected by the laser within the strong peak. The photogenerated centers also emit at 645 nm. Hence, the emission intensity did not change at all during hole formation. Accordingly, we also observed an additional peak in the excitation spectrum on the short wavelength side of the strong ZPL at 600 nm (peak C, Fig. 10) which appeared only after the sample was exposed to the laser for about 15 min. The photogenerated peak at 600 nm (peak C) did not appear all the time and its intensity depended on the laser power, frequency, duration of exposure and spatial location in the material. The new peak at 600 nm is unstable and lasts for ~ 30 min at 10 K and reappears if the sample is exposed to the laser beam again. We were able to burn a hole in peak C also (Fig. 11). This implies that the three peaks at 601 ± 1 nm (A, B and C) are ZPLs belonging to different centers/sites. The light induced peak is not assigned to F_2^+ because its ZPL is expected to be in the near-infrared region. The previous studies indicated that F_2^+ center was mobile [15]. When the mobile center encounters other charges/molecules, a new F-aggregate center is formed whose ZPL happens to be at 600 nm in the current studies. The

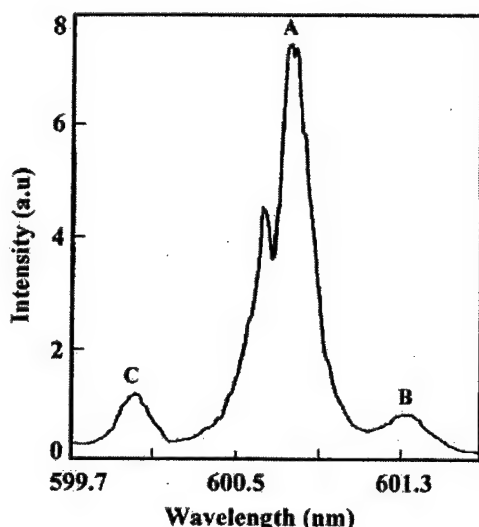


Fig. 10. Excitation spectrum: peak C (a new center) was induced when peak A was excited by the laser. Peak C appeared after a long exposure to the laser beam. It does not appear in all the recordings.

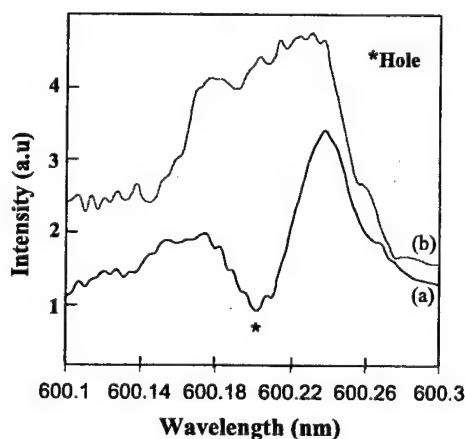


Fig. 11. Excitation spectra: (a) after and (b) before hole burning in peak C. Emission at 645 nm was monitored. Sample temperature was 10 K.

F-aggregate center formation depends on the probability of finding other charges/particles in the vicinity of F_2^+ . Hence that is the reason why we did not observe the induced center (peak C) every time a hole is burned in the ZPL and also depended on the spatial location of the beam in

the material. Emission from all the three centers overlap in the vicinity of the broad band centered at 645 nm. Hence, the lifetime was found to be dependent on the wavelength monitored.

4. Conclusions

In conclusion, we have detected three zero-phonon transitions at 601 ± 1 nm belonging to different centers and spectral holes were burned in all, for the first time. Persistent spectral hole burning was observed up to 40 K. This material is useful for long-term data storage because it retains holes for a long time without any degradation. Holes can be erased by raising the sample temperature to more than 200 K. Laser-induced color center formation has been demonstrated. So far in LiF hole burning was demonstrated at five ZPLs including the previous works [11,12] and four of them are useful for data storage. Thus the optical data storage capacity of LiF is much higher than that known previously for this material. Hole burning in peak C at 600 nm is not suitable for data storage because its appearance is not reliable and depended on spatial location of the beam in the material as well as several other factors mentioned in the previous section.

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Persistent spectral hole burning studies of europium-doped sodium germanate glass

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Abstract

Persistent spectral hole burning has been observed in europium-doped sodium germanate glass. Hole burning efficiency increased 85% when the glasses were made in a reduced atmosphere and hole burning was detected even at room temperature. There is evidence for photochemical as well as photophysical hole burning mechanisms.

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Several types of materials are being characterized for optical hole burning studies because of their potential applications in optical data storage¹. In general rare-earth ion doped crystals² facilitate transient hole burning whereas glasses³ facilitate persistent spectral hole burning. Persistent hole burning mechanism appears to depend on the type of material⁴⁻⁹. In europium doped sol-gel glasses it was due to rearrangement of -OH bonds around the photo-excited ion¹⁰, and in glasses prepared in a reduced atmosphere it was due to the exchange of a charge between the excited ion and the surroundings^{3,11}. To have any practical application the material should facilitate high density hole burning at temperatures higher than those achieved using cryogenics. So there is a need to investigate different materials to identify the ones with better characteristics for hole burning. For this purpose we are investigating sodium germanate glasses. Hole burning was observed in the past only in Pr³⁺ doped germanate glass,¹² that too at 4.2 K. Hole burning in Eu³⁺ doped germanate glass was not reported in the past¹³. Here we are reporting room temperature persistent spectral hole burning in europium doped sodium germanate glass. Another important feature of this sample is that hole burning has been observed even in a sample that was made in ambient air which was not the case with the other melt quenched glasses, like sodium borates and silicates^{3-8,10,11}. Moreover, for this sample there is direct experimental evidence for photophysical hole burning mechanism whereas there was no such evidence for melt quenched glasses in the past.

Sodium germanate glass was prepared with the following composition. Na₂O (21mol%): GeO₂(78 mol%) and Eu₂O₃ (1 mol%). The purity of the chemicals was better than 99.9% and they were obtained from Alfa-Aesar. The chemicals were mixed thoroughly and then melted in a box furnace at 1150°C for an hour in ambient air. We

made glasses in air as well as reduced atmosphere, with and without yttrium co-dopant, a total of four samples. The glass compositions as well as hole burning parameters are summarized in Table 1. Co-doped glasses required melting temperatures of 1250°C. A tube furnace was used to melt the glass in a reduced atmosphere, by passing 90% N₂ + 10%H₂ mixture. The melt was poured into an aluminum mold and allowed to cool to room temperature naturally. It was polished on all sides to minimize scattering. Glasses made in reduced atmosphere have a light tint of yellow color. Hole burning measurements were performed with a broadband dye laser whose linewidth ~60GHz, that was focused to a spot diameter of 27 μm. A power of 5 – 200 mW was used to burn a hole and a power of ~ 1-2 mW to probe the hole. The emission at 612nm was monitored in the excitation spectral recordings.

For the glass melted in ambient air (sample 1) the absorption spectrum revealed only Eu³⁺ peaks (Fig. 1(a)). However when the glass was melted in a reduced atmosphere (sample 3) a strong absorption appeared at 400nm which is due to the presence of Eu²⁺ (Fig. 1(b))³. The broad absorption extended up to 450nm (Fig. 1(c)) when the reduced glass contains the co-dopant Y³⁺ (sample 4). It was known that Eu³⁺ disperses more uniformly in the glass matrix when it was co-doped with Y³⁺^{14,15}. As a result the reduction probability of Eu³⁺ to Eu²⁺ increases and hence the broad absorption extended to the blue region. Fluorescence spectrum revealed the Eu³⁺ peaks at 595, 613, 654 and 705 nm (⁵D₀→⁷F_J (J=1 to 4)) as expected. The ⁵D₀→⁷F₂ group emission features showed strong dependence on the excitation wavelength (Fig. 2) which is a characteristic of fluorescence line narrowing (FLN).

Materials that exhibit FLN are promising candidates for hole burning. Hence we investigated hole burning studies by recording the excitation spectra before and after hole burning. We burned 11 holes in the ${}^7F_0 \rightarrow {}^5D_0$ transition of sample #1, and it retained all the holes. However, the previously burned holes partially refilled. Hole burning was possible up to 77K in samples made in ambient air. A hole depth of 7% was achieved after 10 minutes of exposure with 10mW of power ($1.2\text{kW}/\text{cm}^2$). Typical hole width, Γ_h was $\sim 2.8\text{ cm}^{-1}$ and the ratio of inhomogeneous broadening (Γ_{inh}) to hole width (Γ_h) was ~ 28 . When the glasses were made in ambient air the addition of Y_2O_3 did not make any improvement to either hole burning efficiency or number of holes burned. In fact we could not burn more than four holes and the holes were shallower in the co-doped glass. Hole burning required 15 minutes of exposure with a 180mW beam (intensity is $21.5\text{ kW}/\text{cm}^2$). The reason could be the following. Europium existed only in trivalent form and the hole burning may be due to a photophysical mechanism which is further clarified later on. The addition of yttrium oxide probably added mechanical strength to the glass, thus requiring higher powers to produce a hole. There is no evidence of Eu^{2+} in this glass and hence the possibility of photochemical hole burning was not considered.

However when the glass was melted in a reduced atmosphere there is significant improvement in the hole burning efficiency. A 5 minute exposure to a 10mW laser beam (of intensity $1.2\text{kW}/\text{cm}^2$) burned a hole at 10K, in the reduced glass. However if the reduced glass contains 3mol% Y_2O_3 , then a hole was burned with 2mW beam (intensity $0.24\text{kW}/\text{cm}^2$) after 1 minute exposure. We were able to burn 16 holes in the co-doped glass (Fig. 3(a)), though there was partial refilling of the previous holes. This number could be much higher if a single frequency laser was used. Temporal evolution of the

fluorescence revealed that the hole depth approached saturation in about 25 s (Fig. 3(b)) when the hole was burned with a 2mW laser beam. An analysis of the absorption spectrum revealed that the abundance of Eu^{2+} is high in the co-doped glass (Fig. 1(c)). In other words the presence of Eu^{2+} enhances hole burning efficiency, whose abundance increases in the presence of Y^{3+} . This behavior is similar to that observed in silicate and borate glasses^{3,6,7,11}. This observation supports the photochemical hole burning mechanism, where a charge is exchanged between Eu^{3+} and Eu^{2+} .

Hole burning was detected at room temperature only when the samples were made in a reduced atmosphere. Another interesting spectral feature was observed for the co-doped glass (sample #4). A low temperature excitation spectrum revealed only a hole (Fig. 4(b)). However, a room temperature excitation spectrum revealed a hole as well as an anti-hole (Fig. 4(c)), which was reproducible. This observation supports a photophysical hole burning mechanism. If the environment of the photoexcited ion changes slightly, the crystal field at the ion changes, as a result the position of its energy level shifts slightly, to a lower value in the present case and is represented by a dotted level in the inset (Fig. 4(d)). Hence its absorption (anti-hole) appears at a slightly longer wavelength side but within the inhomogeneous broadening. This is a clear demonstration of photophysical effects. Consequently enhanced absorption occurs at the new frequency (corresponding to the dotted level) and a hole appears at the original frequency (corresponding to the solid level), because the ions do not absorb at the original frequency anymore. This observation indicates that photophysical mechanism also contributes to the hole burning process. However when the sample was maintained at 10K no anti-hole was detected. This could be due to the following two reasons. (1) Anti-

hole appears only when the number of ions undergoing photophysical process exceeds a certain threshold value, depending on the detection system used. For sample#4, that threshold value exceeded at room temperature. (2) Probably the photophysical process was assisted by thermal energy. At low temperatures thermal energy decreases and hence there was no anti-hole in the excitation spectrum (Fig. 4(b)). The hole burnt at room temperature lasted for more than three hours. However when a second hole was burned the previous hole was refilled completely at room temperature.

For the purpose of comparison, hole burning efficiency has been assumed to be proportional to hole depth obtained under similar excitation conditions. An observation of the last column in Table I reveals that the efficiency increased 85% when the sample was melted in a reduced atmosphere (sample #3) when compared to that melted in air (sample #1). Addition of Y^{3+} co-dopant increased the hole depth/efficiency by 38% and the number of holes by 60% (sample #4). This observation is quite opposite to that of sample #2 which was melted in ambient air. Among the reduced samples, the co-doped sample required $15\times$ less radiation dosage (power x time of exposure) to burn a hole. Our studies indicate that both photophysical and photochemical hole burning mechanisms occur simultaneously in the reduced samples of europium doped sodium germanate glass.

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Figure captions

FIG. 1. Room temperature absorption spectra of europium doped glasses. Curve (a) is that of glass melted in ambient air, curves (b) and (c) are those of glasses melted in a reduced atmosphere. The glass composition of samples #1 and #3 (curves (a) and (b)): Na_2O (21mol%), GeO_2 (78 mol%) and Eu_2O_3 (1 mol%); sample #4 (curve (c)): Na_2O (21 mol%), GeO_2 (75%), Y_2O_3 (3mol%) Eu_2O_3 (1mol%). Sharp peaks are those of Eu^{3+} and the broad absorption at 400nm is due to the presence of Eu^{2+} .

FIG. 2. Fluorescence spectra of Eu^{3+} obtained for a glass that was melted in a reduced atmosphere as a function of excitation wavelength. The figure reveals the effect of FLN.

FIG. 3. Curve (a) reveals multiple hole burning observed at 10K in sample #4. Holes were burned with 50mW beam (intensity, $6\text{kW}/\text{cm}^2$) by exposing the sample for 3 minutes at each wavelength. Curve (b) shows the variation of emission intensity during the hole formation. Hole depth saturates in about 25 seconds for 2mW laser power (intensity is $0.24\text{kW}/\text{cm}^2$).

FIG. 4. Excitation spectra of sample #4 obtained (a) before and (b) after hole burning at 10K. Curve (c) obtained at room temperature exhibits hole as well as anti-hole. Inset (d) shows the position of the $^5\text{D}_0$ level before (solid line) and after (dotted level) photophysical hole burning.

TABLE I : Comparison of the salient features of different glasses

S# ^{a)}	mol(%)				atmos. ^{b)}	T _{max} ^{c)} (K)	#holes ^{d)}	dosage ^{e)}	hole depth(%)
	Na ₂ O	GeO ₂	Y ₂ O ₃	Eu ₂ O ₃					
1	21	78	0	1	Air	77	11	50	7
2	21	73	5	1	Air	77	4	1350	5
3	21	78	0	1	N ₂ +H ₂	293	10	25	13
4	21	75	3	1	N ₂ +H ₂	293	16	1	18

^{a)}s# is the sample number.

^{b)}Refers to the melting atmosphere.

^{c)}T_{max} is the maximum temperature at which hole burning was observed.

^{d)}# holes is the maximum number burned at 10K with a 60GHz laser.

^{e)}Dosage is the product of laser power and time of exposure. Relative dosage is given.

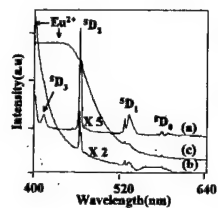


FIG. 1, Kalluru, Journal of Applied Physics

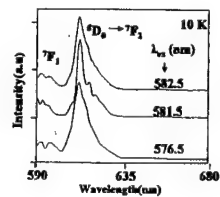


FIG. 2, Kalluru, Journal of Applied Physics

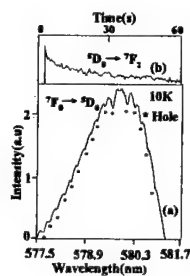


FIG. 3, Kalluru, Journal of Applied Physics

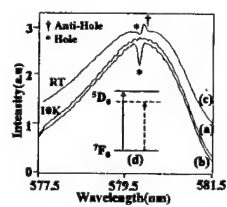


FIG. 4, Kalluru, Journal of Applied Physics

(in the process of communication)

Persistent spectral hole burning in europium doped sodium borosilicate glass^{a)}

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Abstract

Sodium borosilicate glasses doped with Eu^{3+} and Eu^{2+} were prepared. Persistent spectral hole burning was observed up to 250K. Multiple hole burning is possible with moderate laser powers. When the glass composition was modified by adding 5% yttrium oxide to the base glass hole retention capability and efficiency increased. Intensity versus time plot showed evidence of room temperature hole burning.

In the past persistent spectral hole burning was observed in europium doped sodium silicate^{1,2} and borate glasses^{3,4}. The hole burning mechanism depended on the glass composition and preparation methods used⁵⁻⁸. A mW power was enough to burn a hole in the silicate glass whereas several tens of mW power was required to burn a hole in the borate glass. Sodium borate host retains multiple holes without any degradation whereas silicate host does not retain more than one hole at a time. Ricard et al⁹ were able to burn multiple holes in LaAlSi sample but a very high laser intensity was required even to burn a very shallow hole. So we are interested in making a material that permits multiple hole burning at moderate powers. We have investigated a europium doped sodium borosilicate glass to accomplish our objective and are reporting hole burning for the first time to our knowledge.

We prepared sodium borosilicate glasses with the following chemical compositions: (1) Na₂CO₃ (30%), B₂O₃(34%), SiO₂ (34%), Eu₂O₃(2%) and (2) Na₂CO₃(27.5%), B₂O₃(34%), SiO₂(31.5%), Y₂O₃(5%), Eu₂O₃(2%). Such glasses were made in ambient air as well as reducing atmosphere, that is, a total of four samples. Sodium borosilicate glasses were melted at 1450°C. The glass preparation and optical characterization methods are similar to those described previously¹⁰. A medium resolution monochromator fitted with a photomultiplier tube (PMT) was used in the spectral recordings. Some emission spectra were recorded using a CCD (charge coupled device) camera. The remaining experimental details are same as those described elsewhere¹⁰.

The room temperature absorption spectrum revealed sharp Eu³⁺ peaks when the sample was melted only in ambient air (not shown). For samples melted in a reduced

atmosphere a strong absorption appeared in the uv-blue region, extending up to 470nm which was due to the formation of Eu^{2+} . When the sample contained 5% Y_2O_3 the strong absorption extended up to 500nm (Fig. 1) because a larger percentage of europium ions existed in divalent form and to some extent by the defects induced¹⁰ in the glass by Y^{3+} . This happened because Y^{3+} was effective in dispersing the rare-earth ions uniformly in the material^{11,12}. Hence the reduction probability of the rare-earth ions was high in a co-doped glass. The presence of Eu^{2+} was confirmed by the revelation of a broad fluorescence^{13,14} that is peaking at 495nm, under 337nm N_2 laser excitation (Fig. 2(a)). The peak of the fluorescence shifted to 535nm (Fig. 2(b)) (or 580nm (Fig. 2(c)) under 458nm (or 488nm) laser excitation because of spectral overlap arising from Eu^{2+} as well as Eu^{3+} . The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} is a hypersensitive transition and the emission spectral shape depended on the laser excitation wavelength (Fig. 3), due to site to site variations in crystal field, which is a consequence of fluorescence line narrowing (FLN). This confirms the presence of Eu^{3+} in the glass though its sharp peaks did not appear in the absorption spectrum.

Excitation spectrum was recorded by monitoring the fluorescence at 612nm. Hole burning was detected by comparing the excitation spectra recorded before and after hole burning (Fig. 4). Excitation spectrum revealed a hole up to the sample temperature of 250K. However intensity versus time plot of the co-doped sample exhibited a sharp reduction in emission intensity even at room temperature (Fig. 5) which is due to hole burning. At 10K even a mW laser beam was enough to burn a hole. Hole depth of 18% was achieved very easily with 30mW power within 10 minutes of exposure. Inhomogeneous broadening was $\sim 91 \text{ cm}^{-1}$ and the ratio of inhomogeneous broadening to

hole width was about 27. We have burned 16 holes in the material and it retained all the holes (Fig. 6). For the multiple hole burning the sample was exposed to a power of 12mW and the time of exposure was 2 minutes. The number of holes was limited because of the broadband dye laser used in these experiments.

Hole burning mechanism is same as that in silicate and borate glasses^{2,4,10}. Hole burning is due to a charge exchange between Eu^{3+} and Eu^{2+} . In that case the concentrations of Eu^{2+} as well as Eu^{3+} will remain the same before and after hole burning. This argument was supported by the emission spectra of the dopants recorded before and after hole burning, which did not show any variation. Apparently in a sodium silicate host the electrons are easily mobile because the hole was erased even by a laser beam that was not absorbed by the sample. However in a sodium borosilicate glass the coordination of the europium is different from that encountered in sodium silicate glass. As a result the holes are stable in the sodium borosilicate glass and multiple hole burning is possible. At 10K the effect of Y^{3+} is marginal, for example hole depth was 18% instead of 17% (with out Y^{3+}) and a 30s exposure was enough to burn a hole instead of 1minute required for the other sample (with out Y^{3+}). At low concentrations of Eu^{2+} the hole burning efficiency increases with the abundance of Eu^{2+} . Beyond a certain threshold value of Eu^{2+} concentration, the change in efficiency is only marginal. Because of this reason though Y^{3+} was effective in reducing more of Eu^{3+} ions to Eu^{2+} state the enhancement in hole burning efficiency is only marginal and not as high an improvement as that observed in the borate glass¹⁰.

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Figure captions

Fig. 1. Room temperature absorption spectrum of sodium borosilicate glass doped with (a) europium and (b) europium and yttrium. The broad absorption in the blue region indicates the presence of Eu^{2+} in the glass. The sample was melted in a reduced atmosphere.

Fig. 2. Fluorescence spectrum of europium doped sodium borosilicate glass obtained at 10K under different laser excitation conditions: (a) 337 nm N_2 laser (b) 458nm and (c) 488nm Ar^+ laser. Peak of the fluorescence depends on the excitation wavelength due to the presence Eu^{2+} and Eu^{3+} in the sample prepared in a reduced atmosphere.

Fig. 3. Fluorescence line narrowing (FLN) in europium doped sodium borosilicate glass.

Fig. 4. Excitation spectra recorded at 10 K before (a) and after (b) hole burning in europium, yttrium co-doped sodium borosilicate glass. The difference spectrum (c) reveals a sharp hole. The power falling on the sample during hole burning was 23.5mW.

Fig. 5. Time dependence of Eu^{3+} fluorescence intensity during the hole burning at 297K. (a) europium doped glass (b) europium, yttrium doped glass.

Fig. 6. Multiple hole burning. Excitation spectra recorded (a) before and (b) after hole burning. In this experiment the sample was exposed to 12mW and the time of exposure was 2 minutes.

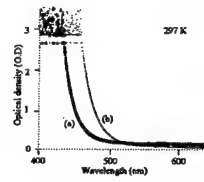


Fig. 1. Kallou

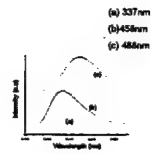


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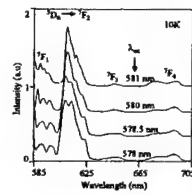


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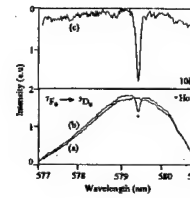


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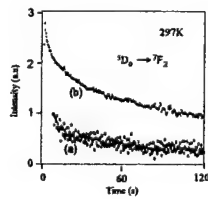


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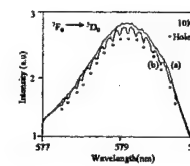


Fig. 6. Kallou

Journal of Luminescence (submitted)
Persistent spectral hole burning in Eu^{3+} , Y^{3+} co-doped sodium silicate glass

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Abstract

Sodium silicate glasses doped with Eu^{3+} and Eu^{2+} were prepared. Persistent spectral hole burning was observed up to 250 K. The photochemical hole burning is due to a charge transfer between Eu^{3+} and Eu^{2+} . When the glass composition was modified by adding 5% yttrium oxide to the base glass spectral inhomogeneous broadening, hole density, hole retention capability and hole burning efficiency increased. Intensity versus time plot showed evidence of room temperature hole burning. Thermal stability of the holes also increased in the modified silicate glass.

PACS: 32.50.+d, 71.23.Cq, 72.80.Ng, 76.30.Kg, 78.40.Ha, 78.55.Hx

Keywords: optical hole burning, zero-phonon transitions, Fluorescence line narrowing, Europium doped sodium silicate glass, photo-reduction of europium.

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1. Introduction

Several types of materials are under investigation for optical hole burning work because of their possible applications in optical data storage. One of the material's requirements is a large ratio of inhomogeneous to homogeneous broadenings. Glasses are easy to prepare and the inhomogeneous broadening encountered in glasses are much higher than those of single crystals. Hence glasses possess certain advantages when compared to others. Mao et al [1] burned a thermally stable hole in aluminosilicate glass that was made in an inert atmosphere. Later Fujita et al [2, 3] prepared europium doped sodium silicate and aluminum silicate glasses in inert/reduced atmospheres and observed hole burning in them up to room temperature. They also found that that hole burning efficiency is higher in a sodium silicate glass than that in sodium aluminosilicate glass, but the former does not retain more holes. Photoinduced reduction of Eu^{3+} was found to be responsible for the hole burning mechanism. Koyama and Suemoto [4] observed wide holes in beta alumina up to 14.6 K and attributed the phenomenon to lattice rearrangement. Nogami et al [5] prepared Eu doped $\text{Al}_2\text{O}_3 - \text{SiO}_2$ glass in a reduced atmosphere and concluded that an electron transfer between Eu^{3+} and defect centers in the Al-O bonds burns a hole. Ricard et al [6] were able to burn 17 holes in LaAlSi sample but large laser intensity was required even to burn a very shallow hole. Nogami et al [7] prepared europium doped sol-gel glasses and found that photoinduced rearrangement of OH bonds was responsible for the hole burning. We are interested in developing materials that facilitate hole burning with low laser intensities and retain more

holes at each spot. To accomplish these objectives we prepared sodium silicate glasses doped with europium. It is easy to burn a hole in this material but it does not retain more holes. To address this problem we are investigating the effect of yttrium oxide on hole burning in europium doped sodium silicate glass. Yttrium was chosen because the previous investigations revealed that it was effective in dispersing the rare-earth ions more uniformly in the glass [8,9].

2. Experimental

We prepared two different mixtures with the following chemical compositions: (1) SiO_2 (48.2%), $\text{NaO}_{1/2}$ (51.8%) and (2) SiO_2 (45.2%), $\text{NaO}_{1/2}$ (48.8%), $\text{YO}_{3/2}$ (6%) where the cationic component percentage is given in the parentheses. To each of the above mixtures $\text{EuO}_{3/2}$ (3%) was added. Here after the resulting materials are called samples 1 and 2 respectively. The purity of the raw chemicals was better than 99.9% and was obtained from Alfa-Aesar. Chemicals were mixed in 8 g batches thoroughly for an hour in a porcelain mortar. The chemicals were poured into an alumina crucible and heated in a box furnace at 1550°C in ambient air for two hours and then cooled to room temperature. The solidified melt was removed from the crucible and crushed mechanically using metal plates. The crushed powder was poured into another alumina crucible and heated for an hour at 1550°C in a tube furnace under flowing gases; N_2 (90%) + H_2 (10%) at 10 PSI. The crucible was taken out of the furnace and allowed to cool naturally. The solidified melt was removed by breaking the crucible. Later on it was polished to get the shape of a rectangular block. The resulting glass is yellowish in color but transparent in the visible region. The samples were cooled in a closed cycle cryostat up to 10 K. A Rhodamine 6G continuous wave dye laser was used for hole burning and

excitation spectral recordings. A medium resolution spectrometer fitted with a photomultiplier tube was used to acquire the spectra. Some emission spectra were recorded using a CCD (charge coupled device) camera. The remaining experimental details are same as those described elsewhere [10].

3. Results and discussion

The room temperature absorption spectrum revealed strong absorption below 500nm and no sharp peaks of Eu^{3+} were detected (Fig. 1). The strong absorption at 400nm was due to the formation of Eu^{2+} in a reduced atmosphere. When the glass was excited by a 488nm Argon ion laser a broad fluorescence was observed in the region 540 to 800 nm (Fig. 2). This confirms the presence of Eu^{2+} in the glass [11-13]. For the reduction purpose Eu^{3+} has to gain an electron from the host glass. Rare-earth ions were known to cluster in a glass, which reduces the probability for reduction. However, in a glass co-doped with Y^{3+} clustering of Eu^{3+} is minimized [8, 9] and hence the reduction probability of the latter increases. Accordingly the absorption slightly increased in sample 2 indicating that more of the Eu^{3+} ions are reduced to Eu^{2+} . Addition of Y^{3+} was also known to create more defects [10] in the material and nonbridging oxygens (NBO) in the glass. This may create a charge imbalance, which is compensated by the reduction of Eu^{3+} to Eu^{2+} because Y^{2+} was not known to occur. Thermodynamic data also supports this argument. The redox equilibrium of europium depends on the affinity of oxygen to the europium. Affinity is estimated from the standard free energy of formation of metal oxide. The formation energy [14] of Eu_2O_3 ($\Delta H_f = -1921.247\text{kJ/mol}$) is comparable to that of Y_2O_3 ($\Delta H_f = -1921.247\text{kJ/mol}$) at 1800K but much smaller than that of SiO_2 ($\Delta H_f = -946.742\text{kJ/mol}$). The reduction ability also depends on the presence of non-bridging

oxygen ions whose concentration increases with the addition of divalent and trivalent ions to the glass. Eu^{3+} is preferentially coordinated by NBO-Na^+ whereas Eu^{2+} is uniformly distributed as a network modifier. As expected laser induced fluorescence spectrum (Fig. 3) revealed Eu^{3+} peaks at 595 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 612 ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 653 ($^5\text{D}_0 \rightarrow ^7\text{F}_3$) and 703nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$). The spectral features such as the number of peaks, their spacing and shape were also found to depend on the laser wavelength used for excitation of the $^5\text{D}_0$ level (Fig. 3). There is a drastic change in spectral features when the excitation wavelength was changed from 575 to 581 nm. In other words the figure reveals site to site variations, which are consequences of fluorescence line narrowing (FLN) effect. The intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ group is sensitive to changes in the environment of the dopant ion. Most of the materials that exhibit FLN also exhibit hole burning.

By monitoring the fluorescence at 612nm and simultaneously sweeping the wavelength of a low power tunable laser a low temperature excitation spectrum was recorded. The excitation spectrum revealed a broad peak at 580nm whose inhomogeneous broadening (full width at half maximum) is 62.4cm^{-1} . A hole was burned even with 0.7 mW laser beam after 60 s of exposure. Hole burning was measured by comparing the low power excitation spectra recorded before and after exposure (Fig. 4). The hole-width is $\sim 2.2\text{ cm}^{-1}$ and the ratio of inhomogeneous to homogeneous broadening is 28 (number of holes at a spot). Hole stability was investigated by a temperature cycling experiment. After burning a hole at 10K the sample temperature was increased to 120K for 5 minutes. Afterwards the sample was cooled back to 10K and an excitation spectrum was recorded again. It turned out that 41% of the hole was refilled. In other words the holes do not have thermal stability. At 10K the holes are lasting for

more than three hours without any change in shape. However, when a second hole was burned (with out changing the laser intensity) at a different wavelength within the inhomogeneous broadening the hole burned previously disappeared. In fact the hole was also erased by a 250mW laser beam at 584nm, which was not absorbed by the sample, after 10 minutes of exposure. To overcome this problem the laser power and time of exposure were reduced for successive holes. Thus we were able to burn three holes and it retained all three holes. A maximum hole depth of 27% was achieved. Intensity (I) versus time (T) plot revealed that 19% hole depth was achieved in 50 s with a focused beam intensity of 7.9 kW/cm^2 . Excitation spectrum revealed a hole up to the sample temperature of 150 K while the intensity versus time recording revealed hole burning up to the sample temperature of 250 K.

In the co-doped glass (sample 2) deeper holes were burned with a relatively low power laser beam. A hole was burned with 0.2mW laser beam after 60 s of exposure. Maximum hole depth achieved was 29%. However, I versus T plot revealed that 21% hole depth was achieved in 50 s with a beam intensity of 2.7 kW/cm^2 . The inhomogeneous broadening, hole width and the number of holes per spot are 74.6 cm^{-1} , 1.92 cm^{-1} and 38 respectively. In a co-doped glass we were able to burn 7 holes whereas only 3 holes could be burned in sample 1 (Fig. 5). A temperature cycling experiment was performed similar to that of sample 1. It was observed that only 21% of the hole was refilled. In other words hole stability increased in the co-doped sample. Excitation spectrum revealed hole burning up to 250 K while I versus T plot revealed hole burning even at room temperature. Hole erasure with the 584 nm laser required ~20 minutes of exposure, which is $2\times$ longer than that required for sample 1. Hole burning efficiency is

expected to be proportional to the hole area [3]. So hole area of the two samples obtained under similar experimental conditions were compared. It turned out that the hole burning efficiency of sample 2 was $2\times$ that of sample 1.

Next we tried to get some insight into the hole burning mechanism in melt grown samples. The fact that hole burning was detected only when the glasses were made in a reduced atmosphere clearly indicates that both Eu^{3+} and Eu^{2+} are required for the hole burning to take place. Additionally defects were also known to be induced in the glass when it was prepared in a reduced atmosphere [10]. There has been some difference of opinion whether the excited ion is exchanging a charge with Eu^{2+} or a defect [2-5]. If the Eu^{3+} gains the charge from a defect (other than Eu^{2+}) then Eu^{2+} concentration increases and hence its emission intensity is expected to increase. On the other hand, if the excited Eu^{3+} ion gains an electron from a nearby Eu^{2+} ion ($\text{Eu}^{3+*} + \text{Eu}^{2+} \rightarrow \text{Eu}^{2+*} + \text{Eu}^{3+}$, where an * indicates photoexcited ion) then the Eu^{2+} ion concentration remains the same and the emission intensity of Eu^{2+} does not change. Eu^{2+} absorption extends beyond 500nm. The 488 nm laser is predominantly absorbed by the Eu^{2+} ions. So, to verify the proposed hole burning mechanism Eu^{2+} emission spectrum was recorded with a CCD camera before and after hole burning. There was no change in the Eu^{2+} emission intensity, which indicated that the charge exchange is between the Eu^{3+} and Eu^{2+} ions only and the defects created in the glass [10] did not directly participate in the charge exchange with the photoexcited ion. According to the above mechanism the number of Eu^{3+} ions also remain the same and hence its emission intensity should not change when excited by a laser that does not produce hole burning. To verify this, europium emission was recorded by exciting with 458nm laser beam that is absorbed by Eu^{2+} as well as Eu^{3+} . The emission spectrum

revealed a broad emission from Eu^{2+} , which was superimposed by sharp peaks of Eu^{3+} . There is no change in the emission spectral intensity recorded before and after hole burning which also supports the proposed mechanism.

Hole stability can be explained with the following arguments. When a hole is being burnt some loosely bound electrons are drifting from Eu^{2+} centers to Eu^{3+} centers. Such an electron drift is produced by the electric field of the laser beam. Again the electrons drifted towards the photo-reduced centers are not strongly bound to the rare-earth ions. As a result these electrons drift away from the hole centers when a second hole is burnt or under exposure to any other wavelength, for example, 584nm. Obviously the glass structure permits the mobility of electrons freely. Hole stability increased in glasses co-doped with Y^{3+} because of the following reason. Some europium ions entered Y^{3+} sites and some did not and the co-ordinations are different for both the cases. As a result europium ions located in the Y^{3+} centers probably have higher photostability than the others. This explains why we are able to burn twice the number of holes in the co-doped glass. An observation of Fig. 1 reveals that a large number of Eu^{3+} ions were already reduced even in a sodium silicate glass (there are no sharp peaks of Eu^{3+}). Addition of Y^{3+} caused only a marginal change in absorption due to the increased reduction of Eu^{3+} to Eu^{2+} . So the hole burning efficiency increased only $2\times$ in the co-doped glass. However addition of Y^{3+} to the sodium borate glass increased the hole burning efficiency $18\times$ because a much larger percentage of the Eu^{3+} ions were reduced in this glass.

4. Conclusions

In conclusion hole burning has been demonstrated in europium doped sodium silicate and europium, yttrium co-doped sodium silicate glasses. The addition of yttrium oxide to the sodium silicate glass increases the hole density, hole burning temperature, hole stability as well as hole burning efficiency. Hole burning is due to photon assisted tunneling of charge between Eu^{3+} and Eu^{2+} located in the vicinity.

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Figure captions

Fig.1. Room temperature absorption spectrum of sodium silicate glass doped with (a) Eu^{3+} and (b) Eu^{3+} , Y^{3+} . The absence of sharp peaks indicates that a large percentage of Eu^{3+} ions were reduced to Eu^{2+} .

Fig. 2. Emission spectrum of Eu^{2+} in sodium silicate glass obtained with 488 nm laser excitation. Sample temperature was 10 K.

Fig. 3. Emission spectrum of Eu^{3+} in sodium silicate glass at 10K observed for different laser excitations.

Fig. 4. Excitation spectra of Eu^{3+} emission obtained (a) before and (b) after hole burning at 579.7 nm in sample 1. Inset (c) shows only the hole spectrum obtained after spectral subtraction. Intensity versus time plot (d) reveals that hole depth reaches saturation in 60 s at a laser power of 10 mW. The sample temperature is 10 K.

Fig. 5. Hole burning spectra of Eu^{3+} : (a) sample 1 and (b) sample 2. In the co-doped glass (sample 2) the number of holes is $2\times$ than that of sample 1.

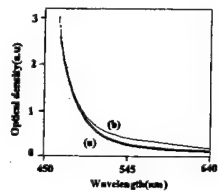


Fig. 1

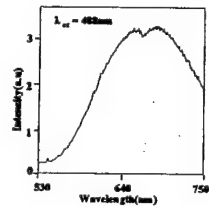


Fig. 2

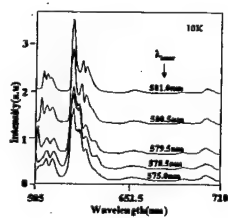


Fig. 3

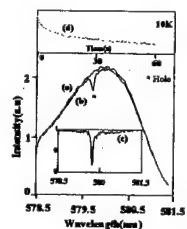


Fig. 4

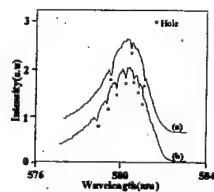


Fig. 5

Manuscript (in preparation)

Persistent spectral hole burning in europium doped sodium tellurite glass

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Abstract

We have prepared sodium telluride glasses doped with europium under different melting atmospheres. Absorption and emission spectra were measured at room and low temperatures. Fluorescence line narrowing has been observed. Persistent spectral hole burning has been observed in the ${}^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} . Multiple hole burning was possible even in a material made in ambient air.

PACS numbers: 42.70.Ln; 78.55.-m; 76.30.kg; 78.55.Qr; 42.62.Fi

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TeO_2 is not stable above 700°C and tends to decompose to TeO and O_2 . So whenever TeO_2 based glasses are heated some oxygen volatilizes from the melt producing intrinsic charged defects (related to oxygen deficiency). Such defects include bonds between two Te atoms or bi-coordinated Te. Such charged intrinsic defects contribute to the disordered structure of glasses and they tend to create attractive sites for rare-earth dopants. The main structural unit of tellurite glasses is a TeO_4 bipyramid; though units with lower coordination of Te are also present. An oxygen vacancy in general is an efficient trap for photoexcited negatively charged electrons and normally acts as a center of radiative recombination. Te-Te bond is longer but weaker than the Te-O bond. Electronegativity of Te is smaller than that of O and therefore the electronic density around Te is higher than for Te in TeO_4 bipyramid. So such units are highly attractive for positive Eu^{3+} because of the following reason. The ability of Te is known to change its valence state. The negative charge and a structural void around Te in defect centers make for an efficient capturer of positively charged Eu^{3+} . Therefore Eu^{3+} will be incorporated in the glass network near to such defects. If the matrix is dominated by TeO_4 then Eu^{3+} does not incorporate well into the glass network. Tellurite glasses form a network structure composed of Te-O. In the melt quenching tellurite can be easily obtained when a modifier such as alkali oxide is added to TeO_2 . In the glassy state the main structural units are TeO_4 trigonal bipyramid and TeO_3 trigonal pyramid. When an alkali oxide is added the concentration of trigonal pyramid increases, that is some TeO_4 units gradually become TeO_3 units.

Persistent hole burning has been observed in oxide glasses doped with inorganic ions and polymers doped with dyes. The hole burning mechanism appears to depend on the glass preparation methods. It was possible to burn multiple holes in a sodium borate glass but it requires slightly higher powers to burn a hole. On the other hand even a mW laser beam was enough to burn a hole in a sodium silicate glass but it does not retain more than one hole at a time. So the glass composition had to be modified to burn more holes. For example europium doped sodium borosilicate glass permits multiple hole burning at moderate powers. Exchange of a charge between Eu^{3+} and Eu^{2+} (or a defect) was found to be responsible for hole burning in some high temperature glasses. A change in the environment of the excited optical center was found to be responsible for hole burning in certain low temperature glasses. However both photophysical as well as photochemical mechanisms were found to be responsible for hole burning in sodium germanate glasses. In any case the hole burning efficiency depends on the host glass composition also. So there is a need to investigate different materials to identify the ones with better characteristics. Tellurium oxide based glasses were not investigated for hole burning in the past. Here we are reporting hole burning in europium doped sodium tellurite glass.

The finished glass has the following composition: Na_2CO_3 (27mol%), TeO_2 (69mol%), Y_2O_3 (3mol%), and Eu_2O_3 (1mol%). The purity of the chemicals was better than 99.9% and obtained from Alfa-Aesar. The chemicals were mixed thoroughly and melted in a box furnace at 850C for an hour in ambient air. We also tried to melt the glass in a reduced atmosphere. The sample turned opaque after a few minutes. During

reduction process some oxygen molecules escaped. As a result defect centers developed which absorb very strongly in the visible region. However when the glass was melted in helium atmosphere a good glass was obtained. The details of glass preparation are similar to those described for other glasses. Room temperature absorption spectrum was recorded using a Cary3E spectrophotometer. Fluorescence was recorded by exciting the material with an Argon ion or a dye laser. For high resolution spectral measurements the sample was cooled to 10K in a closed cycle helium cryostat. A broadband dye laser of 100mW power and 60 GHz linewidth was used to burn a hole and the same laser at reduced power, 1mW was used to probe the hole. A medium resolution spectrometer was used to analyze the fluorescence.

Room temperature absorption spectrum revealed strong absorption in the blue region and the sharp peaks of Eu^{3+} superimposed on it at 470 and 530nm (Fig. 1). To verify whether the broad absorption was due to Eu^{2+} or not another glass was made without europium. It showed a broad absorption up to 450nm. This suggests that the absorption in the blue region is due to the host glass itself. The undoped glass showed a weak intrinsic emission at 530-550nm under blue laser excitation. Fluorescence spectrum of the Eu^{3+} doped sample was recorded by exciting it with a 580nm dye laser. Under dye laser excitation we were able to detect fluorescence at 595 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) and 612nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) (Fig. 2). The fluorescence spectrum showed strong dependence on the pump laser wavelength (Fig. 3), which is due to fluorescence line narrowing. Under 488nm excitation fluorescence was detected at 595, 612 and 700nm. When the sample was excited with 458nm laser (which falls in the broad absorption region), a broad emission occurred at 530-545 and 560-570nm. This suggests that there may be some

Eu^{2+} ions present in the glass, which needs to be confirmed. We made another sample in a helium atmosphere. Its absorption is similar to that of the other sample. But its emission maximum occurs at 640nm. In other words the crystal field strength in this material is much different from that made in ambient air. This is not surprising because the amount of oxygen evaporated from the sample is different when the melt atmosphere is different. The concentration of defect centers (oxygen deficient centers) is different.

To record the excitation spectrum the fluorescence at 612nm was monitored and the laser frequency was swept continuously to cover the $^5\text{D}_0$ absorption peak. The laser power was reduced to $\sim 1\text{mW}$ in the excitation spectral recordings. To burn a hole the sample was exposed to $\sim 100\text{mW}$ of laser power that falls within the absorption peak ($^7\text{F}_0 \rightarrow ^5\text{D}_0$). To reveal the hole the excitation spectra recorded before and after hole burning was compared. At 100mW laser power a time of 60s was enough to burn a hole. Fairly deep holes were burned when the sample was exposed to 15minutes at 300mW . At this power we were able to burn about 14 holes (Fig. 4), and the material retained all the holes. Excitation spectrum revealed hole burning up to 200K. At 10K we were able to achieve a hole depth of $\sim 30\%$ very easily. The inhomogeneous broadening is $\sim 42\text{cm}^{-1}$ and the hole width is 2.8cm^{-1} . The holes were monitored for three hours. There was no change in the hole shape or depth.

69 TeO₂ - 27 Na₂CO₃ -
 3 Y₂O₃ - 1 Eu₂O₃
 Air 60 min 850 C

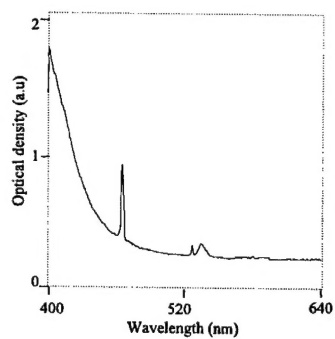


Fig. Room temperature absorption spectrum

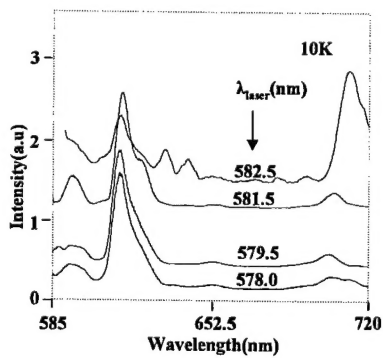
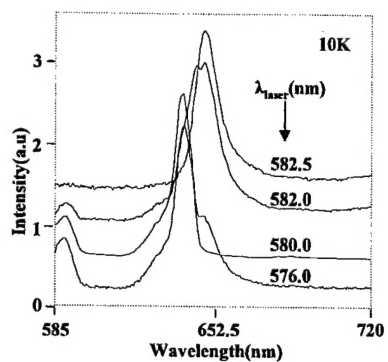


Fig. Fluorescence spectrum of Eu³⁺ as a function of laser excitation wavelength.
 Glass was melted in ambient air.



Fluorescence Spectrum of Eu^{3+} as a function of laser excitation wavelength.
Glass was melted in helium atmosphere.

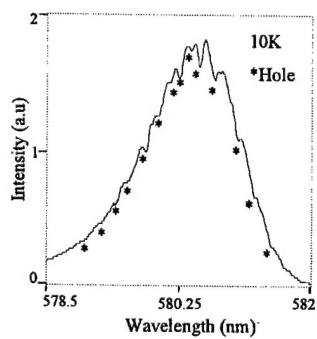


Fig.: Multiple hole burning in Tellurite glass